

LABORATORY PROCEDURES USED IN
RADIOCARBON DATING (C-14)
AT GEOCHRON LABORATORIES

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10 February 1984

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10 February 1984

RADIOCARBON DATING

Radiocarbon dating is widely used for determining the antiquity of archaeological and geological samples back to about 40,000 years ago. The measurement of radiocarbon is also useful as an indicator of the residence time of waters and as an indicator of the chemical authenticity of certain foodstuffs. Radiocarbon dating is conventionally undertaken by the conversion of a carbon-bearing sample to a form suitable for determining its relative C^{14} content by counting the beta-decay events which occur when C^{14} atoms decay to N^{14} . Samples are converted to carbon dioxide which is either used directly or converted to methane, acetylene, or benzene depending on the form preferred by the laboratory. Gases are analyzed in proportional gas counters; benzene is analyzed in a liquid scintillation counter.

RECEIPT OF SAMPLES

LOG-IN AND REPORTING PROCEDURES

When samples are received, they are unpacked and checked against the sample list (when provided). The number appearing on the sample itself is considered authoritative if discrepancies are found. Each sample is then assigned a Geochron sample number from a roll of pre-printed sequentially numbered labels, thus eliminating any chance of two different samples receiving the same number.

Information on each sample is then entered on computer and includes the following:

- GX-xxxxxx (lab number)
- Customer name and affiliation
- Date received
- Customer reference
- Sample description
- Type and condition of sample
- Nature of chemical pretreatment to be applied (if any)

This information is stored on magnetic disk and hardcopy is printed for use as a lab data reference sheet.

All customer-submitted papers, the lab data sheets, and the lab number labels are stored in a folder labeled with the customer's name. This folder is placed with the samples in a container which is labeled on its exterior with the lab numbers of the samples, the customer's name, and the date of receipt. The container is then placed in a storage area to await pretreatment. A card listing the customer, type of analysis to be performed, date received, and Geochron sample numbers is placed on a master sample control board in the main lab office.

As the analyses are completed, the results are entered on the data reference sheet. Computations are made and the final results are printed out on a standard form. All pertinent data are included on this form, which is self-explanatory. The customer folder is then sent back to the office for processing. The original report is proofread against the reference sheet by the office staff. Five photocopies of the completed standard form are made: one is sent to the customer with the original; one is attached to the rest of the material for that particular job in the customer's file; and three are filed sequentially by Geochron sample number in archives stored, for safety, in three separate locations.

The original report, one photocopy, any correspondence, and the invoice are sent together to the customer by first class mail. The file containing the information from the completed job is stored in an alphabetical system by customer's name and affiliation.

PRETREATMENT

Samples are generally processed in order by lab number. When a sample is due for processing the customer's sample identification is again checked against our lab number. The sample then proceeds through pretreatment identified only by its GX-xxxxx (lab-number) label.

The nature of the pretreatment applied for contaminant removal depends mainly on the type of sample material. Our pretreatments are essentially the same as those used by many other radiocarbon dating labs. In general, most organic samples from archaeological or geological contexts are given sequential treatment with dilute acid and dilute base solutions in order to remove, respectively, contaminant carbonates and humates.

Certain materials, such as barium carbonate precipitated from groundwater, need no pretreatment and are analyzed directly.

PREPARATION OF COUNTING GAS

Samples are converted to carbon dioxide by combustion in pure oxygen or by acid hydrolysis. The carbon dioxide is purified and collected by passing through a series of cryogenically cooled traps. Geochron Labs analyzes samples in the form of methane which is prepared by reacting the carbon dioxide with hydrogen at 475°C in the presence of a ruthenium catalyst.

Upon completion of the reaction the methane is purified and separated from excess hydrogen and water of reaction by passing through a series of cryogenic traps which remove water, trap methane, and allow the hydrogen to be vacuumed away. The methane is then transferred to a vacuum flask for storage of the sample gas. The flask is labeled with the lab number, the customer name, dates of reaction, and the volume of methane. The flask is then transferred to the counting room to await loading into one of several proportional counters.

DETERMINATION OF C¹⁴ ACTIVITY

Samples of methane are counted in proportional counters especially designed for the detection of C¹⁴ decay events. The counters are shielded in lead and are surrounded by annular guard counters operating in anticoincidence with the sample counters in order to reduce external radiation background to very low levels.

The sample is counted for C¹⁴ beta activity for at least 1200 minutes, longer if activity is very low.

Ages are calculated by comparing the beta activity of the sample to that of the international standard, NBS oxalic acid (SRM-4990). Calculations used are identical to those outlined in Stuiver and Polach, "Reporting of ¹⁴C Data", Radiocarbon, 19(3):355-363, 1977.

Utilizing the accepted half-life of C¹⁴ of 5570 years the age is calculated as follows:

$$\text{AGE} = (\text{mean-life of C}^{14}) * \ln \frac{\text{Sample activity}}{\text{Standard activity}}$$

where the mean life of C¹⁴ is 8036 years and the standard activity has been normalized to the assumed activity of wood formed in the years A.D. 1950.

The percent modern notation reported for geochemical samples is calculated simply as:

$$\% \text{ modern C}^{14} = 100 * \frac{\text{Sample activity}}{\text{Standard activity}}$$

The error assigned to the age assessment takes into account the uncertainty due to the random nature of C¹⁴ decay in the sample, the error due to background count fluctuations in the proportional counters, and the precision with which the activity of the standard is known.

BACKGROUND, STANDARD, AND C¹³ MEASUREMENTS

Measurement of the background radiation flux in the counters is necessary in order to account for detected radiation which is not due to C¹⁴ decay events. The background count-rate is determined by counting a methane sample prepared from very old marble which no longer contains detectable C¹⁴. A background measurement is made in each counter approximately every eighth day.

Standard activity is determined by periodic counting of methane prepared from the original NBS oxalic acid standard (SRM-4990) or the newly issued replacement standard, NBS Research Material RM-49.

The value used for the modern standard in the age calculation is actually 95% of the observed activity of the standard normalized for isotopic fractionation effects to a delta C¹³ value of -19‰ wrt PDB.*

Precise dating requires that the C¹⁴ activity of the sample be corrected for possible isotopic fractionation. This is also done by measuring the C¹³/C¹² ratio and correcting the C¹⁴ content accordingly. The fractionation of C¹⁴ relative to C¹² is considered to be twice that of C¹³ relative to C¹². Samples are normalized to a C¹³ value of -25‰ wrt PDB** as follows:

$$\text{Samp. activity (C}^{13} \text{ corrected)} = \text{Samp. activity (uncorrected)} * \left(1 - \frac{2(25 + \text{sample delta C}^{13})}{1000}\right)$$

** C¹³ measurements are made on a small aliquot of the sample gas by analysis in a mass-spectrometer. The results are reported in delta notation relative to a standard known as PDB. The calculation of delta values is as follows:

$$\text{delta C}^{13} \text{ sample o/oo} = \left(\frac{\text{C}^{13}/\text{C}^{12} \text{ sample}}{\text{C}^{13}/\text{C}^{12} \text{ PDB}} - 1 \right) * 1000$$

where the ratio of C¹³/C¹² in the PDB standard is 0.011237.

AGE REPORT FORM

The radiocarbon age of each sample is reported on a standard form (see Appendix 1). All pertinent data is included on the form and is self-explanatory. Two copies of this report are sent to the customer, one copy is placed in the customer's file, and three copies are bound in permanent logs and stored at Geochron and other locations for safety.

The customer's file containing all documentation is then filed by customer name or affiliation in a central file system.

Any excess sample is labeled with its lab number and is archived for possible future reference.

Introduction

Stable Isotope Ratio Analysis (SIRA) is a precise measurement of the abundance ratio of two stable isotopes of a particular element. Many elements have two or more stable isotopes which occur in nature. Since the isotopes of a particular element have slightly different properties, they may enter into chemical reactions at different rates. As a result, natural processes have induced large variations in the isotopic composition of some elements, such as carbon, oxygen, nitrogen, and sulfur. Measurement of these variations can give information about geological processes or about the origin of the material analyzed.

The basic methods of sample handling, documentation, instrumental analysis, calculation, and record keeping are similar for all types of SIRA performed at Geochron Laboratories, and can therefore be discussed in general terms. The major differences lie in the methods of sample preparation for the individual elements to be analyzed and the particular type of sample materials to be analyzed. These will be discussed separately.

Documentation of Samples

When a sample is received at Geochron Laboratories, the client's sample number, attached to the sample, is checked against the letter of transmittal, whenever possible, to insure proper agreement. The sample is then given a laboratory sample number in Geochron's sequential sample numbering system. The numbers for SIRA samples are preceded by the letter "R" which indicates that the samples are for SIRA. The "R" prefix is further preceded by another letter or letters denoting the particular elements for which SIRA is to be performed, "C" for carbon, "N" for nitrogen, "O" for oxygen, "S" for sulfur. For example, the prefix "SR-" denotes a sample for sulfur SIRA, while "COR-" denotes a sample (such as a carbonate) for both carbon SIRA and oxygen SIRA.

The SIRA sample number is affixed either to the sample or the sample container, or both, and it is also listed alongside the client's sample number on the letter of transmittal. Thereafter, during all subsequent processing, analyses, and storage of the sample, only the Geochron number is used. At the same time the sample is given a laboratory sample number it is also logged in on a six-copy analytical report form. The information listed on the form at this time includes the client's name and address, the date the sample was received, any reference to the sample received (letter of transmittal, purchase order, job number, etc.), the client's sample number, and the Geochron sample number. At this point the fifth copy of the form is detached and is used as the laboratory work sheet. A brief description of the sample is written on this sheet, as well as the analytical result when it is completed.

The five remaining copies of the report form, along with the letter of transmittal, purchase order, and any other relevant accompanying documents are put into a work file with the client's name on it. This work file is kept with the samples and the work sheet until the analytical work is completed.

Analytical Procedures

The general analytical procedures and techniques used by Geochron Laboratories are similar to those used by most other laboratories around the world which are engaged in SIRA work.

Sample Preparation. Most of the samples received for SIRA work are immediately suitable for the preparation and analysis of the particular element involved. In some instances a particular mineral or material must first be separated from a bulk sample. Because of the large number of possible bulk sample materials, and the various components to be separated from them, it is not possible to detail separation procedures here. Suffice it to say that there are usually no great difficulties along these lines. Where problems do arise, they are most often due to insufficient bulk sample size, or to the general unsuitability

of the particular sample material.

All samples are analyzed in gaseous form. Carbon and oxygen samples are analyzed as carbon dioxide. Sulfur samples are analyzed as sulfur dioxide. Nitrogen samples are analyzed as nitrogen gas. The samples are converted to the appropriate gas by the generally accepted procedures used in SIRA work throughout the world.

Carbon: Samples of organic carbon from hydrocarbon samples, and graphite in rocks, are combusted at 850°C in a pure oxygen atmosphere. The gases are recirculated over CuO , also at 850°C , for 10 minutes to insure complete combustion. The pure carbon dioxide gas is cryogenically separated from the resultant mixture of carbon dioxide, oxygen and water vapor.

Samples of carbonate carbon are prepared by hydrolyzing the carbonate in vacuo with dilute acid, and the resultant carbon dioxide is, again, purified cryogenically.

Nitrogen: At the present time, Geochron Laboratories is equipped only to analyze pre-prepared samples of pure nitrogen gas.

Oxygen: Samples of carbonate oxygen are prepared by reacting the carbonate, in vacuo, with 100% phosphoric acid, at 50°C , and the resultant gas purified cryogenically.

Samples of water oxygen are prepared by equilibrating 3 ml. of the water sample with about 5 cc STP of tank carbon dioxide in a sealed container at 25°C . The equilibrated carbon dioxide gas is then withdrawn and purified for analysis.

Sulfur: Sulfide sulfur and native sulfur samples are combusted in a stream of flowing oxygen at 1300°C and the resultant sulfur dioxide gas purified cryogenically.

Sulfate sulfur samples are prepared by reacting the sulfate with a boiling mixture of hydrochloric, hydriodic and hypophosphorous acids to release hydrogen

sulfide gas, which is passed through a solution of cadmium acetate to precipitate the sulfur as cadmium sulfide. The cadmium sulfide is filtered, dried and then combusted as any other sulfide sample.

Analysis

The gas analyses are performed on a specially designed dual-inlet, double collecting isotope ratio mass spectrometer. In practice, the actual ratios of the isotopes of interest is not measured directly, but rather the isotope ratio in the sample gas is measured in comparison to that of a gas working standard of known isotopic composition. In this way small natural variations in the isotopes of interest can be much more accurately and precisely measured than would otherwise be possible. This method of analysis avoids many possible sources of instrumental error since they are self-cancelling. Some sources of error due to mixing of sample gases and isotopes do occur in the mass spectrometer. When necessary these are measured and corrected for in the final calculations using the commonly accepted procedures for this type of work.

The final SIRA results are reported in terms of the relative difference (δ value) in parts per thousand (termed per mil, and denoted by the symbol o/oo) of the isotopic ratio of the sample compared with that of an internationally-accepted standard of defined isotopic composition. Using sulfur as an example, the calculation is as follows:

$$\delta S^{34} \text{ o/oo} = \left[\frac{S^{34}/S^{32} \text{ sample}}{S^{34}/S^{32} \text{ standard}} - 1 \right] \times 1000$$

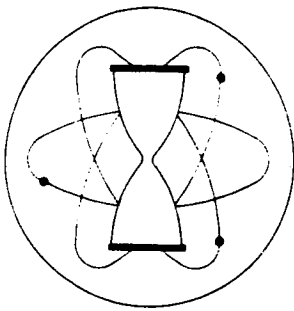
Where: $S^{34}/S^{32} \text{ standard} = 0.0450045$, the internationally accepted value of S^{34}/S^{32} in troilite in meteorites.

The particular standard against which each SIRA analysis is reported by Geochron Laboratories is noted on the report form, and the isotopic composition of each standard is given at the bottom of the report sheet, along with the method of calculation just described.

The analytical data from the mass spectrometer is automatically recorded on paper tape by a desk-top computer which is an integral part of the instrument. This tape is labelled with the Geochron Laboratory number for the sample, the working standard against which the analysis was made, the isotopes analyzed, the date of the analysis, and the initials of the analyst. All calculations are also performed on the calculator, using programs stored in it, and are also recorded on the tape. The final analytical result for each sample is then entered on the work sheet.

When the analysis is complete, the information from the work sheet is typed on the remaining five copies of the report form, which is then checked for accuracy against the work sheet. The first three copies (original and first two carbons) of the work sheet are then forwarded to the client along with the appropriate cover letter and the invoice for the work performed. The fourth copy of the report sheet is placed in the client's permanent file, along with the laboratory work sheet, a copy of the invoice, a copy of the cover letter, and all the other relevant papers received. The paper tape with the analytical data is put on permanent file by laboratory sample number. The fifth copy of the final report is permanently filed, in sequence by sample number, in a record book of all analyses.

Excess sample material which can be conveniently stored without special provision for preservation is permanently stored. Even when the client requests return of excess material, a small amount is usually retained in storage for possible future reference.



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GEOCHRON LABORATORIES DIVISION

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RADIOCARBON AGE DETERMINATION

REPORT OF ANALYTICAL WORK

Our Sample No. GX- 10230

Date Received: 03-23-84

Your Reference:

Date Reported: 04-02-84

Submitted by: Law Engineering Testing Co.
2749 Delk Road, S.E.
Marietta, GA 30067

Sample Name: MW2. Ponce Waste Facility, Puerto Rico. (EPA ID # PRD 980594709).
Job # GS3223, Work Order #11693.

AGE = (53.0 +/- 1.3)% of the modern standard activity.
(7.19 +/- 0.18) dpm/g Carbon.

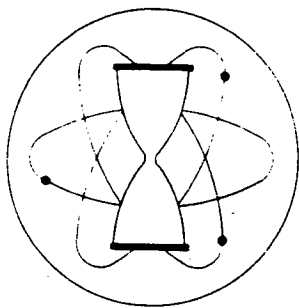
Description: Barium carbonate precipitated from water.

Pretreatment: The barium salt precipitate was rapidly vacuum filtered and immediately hydrolyzed, under vacuum, to recover carbon dioxide from the barium carbonates for the analysis. C-13 analysis was made on a small portion of the same evolved gas.

Comment:
Raw "age" is 5100 +/- 200 C-14 years B.P.

$\delta C_{PDB}^{13} = -9.0 \text{ ‰}$

Notes: This date is based upon the Libby half life (5570 years) for C^{14} . The error stated is $\pm 1 \sigma$ as judged by the analytical data alone. Our modern standard is 95% of the activity of N.B.S. Oxalic Acid.
The age is referenced to the year A.D. 1950.



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RADIOCARBON AGE DETERMINATION

REPORT OF ANALYTICAL WORK

Our Sample No. GX- 10231

Date Received: 03-23-84

Your Reference:

Date Reported: 04-02-84

Submitted by: Law Engineering Testing Co.
2749 Delk Road, S.E.
Marietta, GA 30067

Sample Name: MW3. Ponce Waste Facility, Puerto Rico. (EPA ID # PRD 980594709).
Job # GS3223, Work Order #11693.

AGE = (10.1 +/- 1.2)% of the modern standard activity.
(1.37 +/- 0.16) dpm/g Carbon.

Description: Barium carbonate precipitated from water.

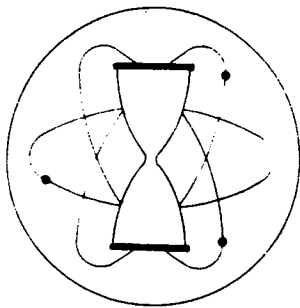
Pretreatment: The barium salt precipitate was rapidly vacuum filtered and immediately hydrolyzed, under vacuum, to recover carbon dioxide from the barium carbonates for the analysis. C-13 analysis was made on a small portion of the same evolved gas.

Comment:

Raw "age" is 18400 +/- 950 C-14 years B.P.

$\delta C_{PDB}^{13} = -5.1$ ‰.

Notes: This date is based upon the Libby half life (5570 years) for C¹⁴. The error stated is $\pm 1 \sigma$ as judged by the analytical data alone. Our modern standard is 95% of the activity of N.B.S. Oxalic Acid.
The age is referenced to the year A.D. 1950.



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RADIOCARBON AGE DETERMINATION

REPORT OF ANALYTICAL WORK

Our Sample No. GX- 10232

Date Received: 03-23-84

Your Reference:

Date Reported: 04-02-84

Submitted by: Law Engineering Testing Co.
2749 Delk Road, S.E.
Marietta, GA 30067

Sample Name: MW4. Ponce Waste Facility, Puerto Rico. (EPA ID # PRD 980594709).
Job # GS3223, Work Order #11693.

AGE = (4.9 +/- 0.6)% of the modern standard activity.
(0.66 +/- 0.08) dpm/g Carbon.

Description: Barium carbonate precipitated from water.

Pretreatment: The barium salt precipitate was rapidly vacuum filtered and immediately hydrolyzed, under vacuum, to recover carbon dioxide from the barium carbonates for the analysis. C-13 analysis was made on a small portion of the same evolved gas.

Comment:

Raw "age" is 24250 +/- 940 C-14 years B.P.

$\delta C_{PDB}^{13} = -3.8$ ‰.

Notes: This date is based upon the Libby half life (5570 years) for C¹⁴. The error stated is $\pm 1 \sigma$ as judged by the analytical data alone. Our modern standard is 95% of the activity of N.B.S. Oxalic Acid.
The age is referenced to the year A.D. 1950.